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SPECTROPHOTOMETRIC USES OF CHLORANILIC ACID AND ITS METALLIC SALTS

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Chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) and particularly a number of its metallic salts form a chemical series that is a new and important addition to the list of analytical reagents. This series, when coupled with spectrophotometric techniques, can aid the analyst immeasurably in coping with a significant segment of the large, complex multitude of analytical needs.

Uses

Although the reactions of chloranilic acid with metal cations were investigated as long ago as 1843 (1), the field remained inactive until the work of Barreto in 1945 (2). Since that time the publications by Tyner in 1948 (3), Coutinho and Almeida (4) in 1951, and Bertolacini and Barney (5,6,7) in 1957 and 1958 have stimulated renewed interest in chloranilic acid and, particularly, in its various metal salts.

Free chloranilic acid is generally used in the determination of polyvalent metal cations, while the metal chloranilate salts find their best application in the determination of various anions. Table I, which summarizes some of the more important uses of these compounds, indicates their broad usefulness. They have been employed in work as widely divergent as the determination of the calcium titer in blood serum (8,9) and in plant tissues (3) to the determination of molybdenum in plutonium alloys (16).

Analytical Procedures

There are a variety of techniques available utilizing chloranilic acid and its salts for analytical purposes. Although the majority are dependent on the spectral absorbency of the purple-colored acid chloranilate ion, there are enough significant differences among the methods to warrant further description.

Method A.—The first method, in order of simplicity as well as chronology, is the gravimetric determination of a cation such as calcium by its quantitative precipi-

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TABLE I

Reagent	Eastman Organic Chemical Number	Species Detected	Method[a]	Reference
Chloranilic acid	4539	Ca^{+2}	A	2,10,11
		Ca^{+2}	B	2,3,10,11,14,20
		Ca^{+2}	D	8,14
		Zr^{+4}	C	11,17
		Mo^{+6}	C	16
		Zn^{+2}	B	24
		Sr^{+2}	B	15,24
		Ba^{+2}	B	15,24
Barium chloranilate	7508	SO_4^{-2}	E	5,7,20,23
Lanthanum chloranilate	7629	F^{-1}	E,C	19
		PO_4^{-3}	E	22
Mercuric chloranilate	7504	Cl^{-1}	E	6,7
Silver chloranilate	7838	Cl^{-1}	E	4,6
Sodium chloranilate	8223	Ca^{+2}	D	9
		[Pb]	D	27
Strontium chloranilate	7633	F^{-1}	E	7
Thorium chloranilate	8257	F^{-1}	E,C	18

[a]This column refers to the general methods used as described in the following section; the letters refer specifically to the section on Analytical Procedures.

tation as an insoluble salt, using excess chloranilic acid (H_2Ch).

$$Ca^{+2} + H_2Ch \longrightarrow CaCh \downarrow + 2H^+$$

The measurement may be either simply by weight (2,10,11) or, as in one refinement, by the use of polarographic techniques (12,13).

Method B.—A popular method is one which depends on the quantitative loss of absorbency of a solution of excess chloranilic acid of known strength by precipitation of an insoluble chloranilate by calcium (3,10,14), or strontium (15), or the like.

$$Ca^{+2}Y^{-2} + 2H_2Ch \longrightarrow H_2Ch + CaCh \downarrow + H_2Y$$

Centrifugation is recommended by recent authors over filtration to obtain a more accurate reading of the residual absorbency of the supernatant liquid.

Method C.—Another method makes use of the absorbency of a highly colored complex formed by chloranilic acid with such cations as molybdenum (16) and zirconium (17). Readings of absorbency are made at 350 mμ as compared to 520-550 mμ for

$$H_2Ch + Zr^{+4} \longrightarrow \left[ZrCh\right]^{+2} + 2H^+$$

chloranilic acid. A novel modification of this procedure is one using a complex of a metal chloranilate salt such as lanthanum (19) or thorium (18) with a specific anion such as fluoride to give a highly colored complex species having an absorbency at a specific wavelength. The sensitivity of this method for the fluoride ion is of high order; Hensley and Barney (18) have reported that as little as 0.01 ppm. can be detected using thorium chloranilate.

Method D.—In still another procedure, and one that is particularly useful in the biological field, a cation, such as calcium, is precipitated as the insoluble chloranilic acid salt, which is isolated either by filtration or by centrifugation. The equivalent free chloranilate ion is then regenerated from the precipitate by use of a sequestering agent (such as ethylenedinitrilo tetraacetic acid) or a strong acid (such as hydrochloric acid) (8,9,14). The regenerated chloranilate ion content is read spectrophotometrically,

$$H_2Ch + Ca^{+2}Y^{-2} \longrightarrow CaCh \downarrow + H_2Y$$

$$CaCh + EDTA\text{-}Na_4 \longrightarrow Na_2Ch + CaEDTA\text{-}Na_2$$

giving the procedure a high degree of accuracy.

An interesting modification (27) of this is the procedure which converts lead to a soluble anion complex (26) and absorbs this complex on a strongly basic ion-exchange resin. This is eluted with distilled water, the pH is adjusted, and the eluate is then treated with sodium chloranilate as in Ferro and Ham's method (8,9) for calcium.

Method E.—The final general method, which is also the most recent, is one which may become the most important of all the analytical uses of chloranilic acid salts. This method, pioneered by Bertolacini and Barney (5,6,7), is used for the determination of various anions and depends on the formation of a highly insoluble salt of the anion with the cation from the chloranilic acid salt, thus releasing the intensely colored acid chloranilate ion (HCh^-) in direct proportion to the amount of anion originally present. For the following typical reaction

$$Ag_2Ch + 2Cl^- + H^+ \longrightarrow HCh^- + 2AgCl \downarrow$$

to proceed quantitatively, the metal chloranilate (Ag_2Ch) must be more soluble than the metal anion salt (AgCl). On the other hand, the metal chloranilate must not be too soluble or the blank colors will be too intense. The choice of pH and solvent system is very important, since the success of the method is directly dependent on the proper relationships of the solubility products as shown by the example of Bertolacini and Barney (5) in the following section on Preparation and Properties.

sorption in the 520-555 mμ region in the visible spectrum when present in a strongly acid environment. More recently, it has been shown (7) that chloranilic acid solutions exhibit an even sharper and particularly intense absorbence peak in the ultraviolet region at 290-340 mμ.

The intensity of the spectral absorption is greatly dependent on pH as well as the choice of solvent. A pH of about 4, maintained by buffering, is favored for most work in the visible spectrum (5), but special care must be observed if biological systems are being investigated (8). In general, in ultraviolet work, it has been found that an alkaline pH from 9-10 provides the maximum sensitivity (7). However, Bertolacini and Barney (7) found that, although the alkaline pH provided greater sensitivity for measuring chloranilate, an acid pH is more useful because of the excessively high blanks produced in the alkaline ranges.

Purity Requirements

Purity of the reagents is a sufficiently important consideration to warrant separate mention. Even though the synthetic procedures may appear to be simple, many controls must be employed to assure a high-quality reagent. Failure to adhere to strict stoichiometry in preparing the reagent can result in two possible major errors in the analytical results obtained. First, care must be taken to avoid excess chloranilic acid in the reagent or the blank will be excessively high. Because of the stability of the properly prepared reagent, only one blank must be read for each bottle of reagent. Under normal conditions, there is no deterioration. If, on the other hand, excess cation be present as a soluble salt, the competition between the two species of divergent solubility properties would result in grossly inaccurate results.

Conclusions

It is readily apparent that some of these procedures may offer no clear improvements over existing methods. However, many applications, particularly in the field of the detection of anions by metathesis with chloranilate salts, appear to offer significant advantages. Ion-exchange resins or masking techniques can be used to achieve the required degree of specificity. The sensitivity of the chloranilate methods generally is excellent and can be controlled by varying pH, solvent, temperature, and the spectral region chosen for the determination. Both the rapidity and the reproducibility with which determinations can be made are excellent. As a result of these attributes, spectrophotometric determinations using chloranilic acid and its metallic salts show great promise of replacing some of the older, more cumbersome techniques.

Availability

As noted in Table I, chloranilic acid is available as chemical 4539 both in an Eastman Practical and an Eastman grade of purity. The metal chloranilate salts are available from stock under their respective Eastman Organic Chemical numbers. Other metal chloranilates are being investigated and will be made available on a custom basis or from stock if popular interest appears to warrant it.

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